LEWIS GRANT
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23P.

SEMI-ANNUAL REPORT

STUDY OF STAEBLER-WRONSKY DEGRADATION EFFECT IN a-Si:H BASED P-I-N SOLAR CELLS

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(NASA-CR-182564) STUDY OF STAEBLER-WRONSKY DEGRADATION EFFECT IN A Si:H BASED P-I-N SOLAR CELLS Semiannual Report (Arkansas Univ.) 23 p CSCL 10A G3/44 N88-25970 Unclas 0149039

NASA-Lewis Research Center

Grant No. NAG 3-802

July 1988

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ACKNOWLEDGEMENT

This report is prepared by H. Goh. The results reported here have been contributed by two graduate students, H. Goh and K. Ng. Dr. G. Blyholder and Dr. Pienta of the Department of Chemistry provided assistance and usage of the FTIR and UV-visible spectroscopy machines. The ultrahigh vacuum deposition system built under this grant to deposit a-Si:H films utilized a lot of existing equipments and facilities belonging to Prof. W. Brown. Much assistance was also given by Dr. Khaliq.

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OBJECTIVE

To improve the stability and efficiency of thin solar cells with emphasis on a-Si:H devices. In our last semi-annual report (Dec 1987) [1], we basically break down the project into three main phases. The first involves designing and building an UHV glow discharge system; the second involves making good quality films and eventually efficient cells; finally the third will be the analytical phase.

STATUS REPORT

On May 15th, 1987 the grant was awarded. Ordering of equipments and materials began. On August 1st, 1987 we started building the system; by the beginning of December the entire system was in place. Leak checking procedures followed. The system was leak checked using a Dycor residual gas analyzer (RGA) and helium as a trace gas. At the same time, the system was monitored for its leak rate over time.

The first 'dummy run' was made on December 9th, 1987. An aluminum foil and a both sides polished P-type silicon wafer were used as substrates. To our dismay, we found that the films had a lot of pinholes. Later, it was found that the problem was due to the reflected power. From December 15th, 1987 to January 15th, 1989, we worked with GSI in Colorado to remedy this problem.

From January 28th, 1988, we started on the full-factorial experiment [2]. The different physical characteristics of every system and the many factors involved, made finding the 'correct' parameter values difficult. Thus the need to know the optimum parameters arose. Our primary goal from this experiment was to find the optimum parameters of the built system,

although this experiment will also furnish more information.

We believe that the bulk i-layer is the first most important problem to be dealt with, and the full-factorial experiment should help us tackle this problem. To the best of our knowledge, there is no published work on optimization of this a-Si:H i-layer. This full-factorial experiment is a structured approach based on statistical design and analysis of the experiments. This approach will provide data on the interaction effects (if any), the vicinity of the optimum points, and an equation on the interaction effects.

FTIR, visible spectrophotometry, photo- and dark conductivity, and film thickness measurements are then made on the samples. They provide information on the ratio of the SiH to SiH_2 bonds density, the Tauc band-gap values, the photo-generations, density of states, etc. FTIR measurements are made on a-Si:H deposited on both sides polished p-type (100) wafers while the spectrophotometry, conductivity, and thickness measurements are made on a-Si:H deposited on Corning 7059 glass. Conductivity measurements involve contacts. Various types of contacts are investigated. They include thermally evaporated indium, aluminum, pure silver, and brushed-on silver paint.

Full-Factorial Experiment

Traditional experiment design has often been conducted haphazardly, with "change one variable at a time, and keeping all the others constant", as the single unifying principle. This can be known as one-at-a-time type experiments. In fact this method is not only inefficient, it is rather incomplete in terms of information obtained. On the other hand, a formal

experimental plan, consisting of a sequence of structured experiments (based on statistical principle) is far more likely to produce a maximum of data, with a minimum expenditure of effort and resources.

There are a number of varying factors involved, namely, substrate temperature, deposition pressure, gas flow rate, RF power, feedgas concentration, frequency, and electrode spacing. The specifications on the feedgases are: silane 99.999% pure, diborane 99.995% pure, and phosphine 99.999% pure. No diluent is used. The frequency of the RF power is fixed at 13.56 MHz, and the electrode spacing is also fixed at 1.11" (± 0.010"). Thus, the experiment is conducted with variation of the first four parameters: substrate temperature, pressure, gas flow rate, and RF power.

Next a choice on the ranges of the parameters is made; this will determine the domain of our experiment:

Substrate Temperature	:	230	to	250	°C
Deposition Pressure	:	500	to	600	mT
Gas Flow Rate	:	30	to	45	sccm
RF Power	:	21.6	to	30.8	mW/cm^2
		(3.5	to	5 W;	$area=162.15cm^2$)

The higher end of the ranges are designated with a (+) sign, and the lower end of the ranges are designated with a (-) sign. The experiment will be two-level. Since there are four variables, there will be two to the power of four or sixteen experiments to run. The values of the parameters used to perform the experiments are (-,-,-,-), (-,-,-,+), (-,-,+,-) ..... (+,+,+,+) not in that order. In fact, to reduce error bias the experiments are randomized. On the next page, there is the computational table where X1 represents the first variable, X2 the second, X3 the third, and X4 the

fourth. X1X2 represents the possible interaction of the two, while X1X2X3 represents the possible interaction of the three and so forth. These products (interaction possibilities) are used in later computations.

Another value, chosen midway between the higher and the lower of the ranges and designated with a (0) sign (not listed in the computing table), is used to determine the curvature effect. Thus the (0) values for substrate temperature, deposition pressure, gas flow rate, and RF power are 240 °C, 550 mT, 37.5 sccm, and 26.2 mW/cm^2 respectively. Four such experiments are spaced evenly among the previous sixteen runs. To reduce experimental and measurement errors, another similar set (i.e. another twenty runs) will be repeated. Figure (1) below shows an example of a curvature effect between two factors.

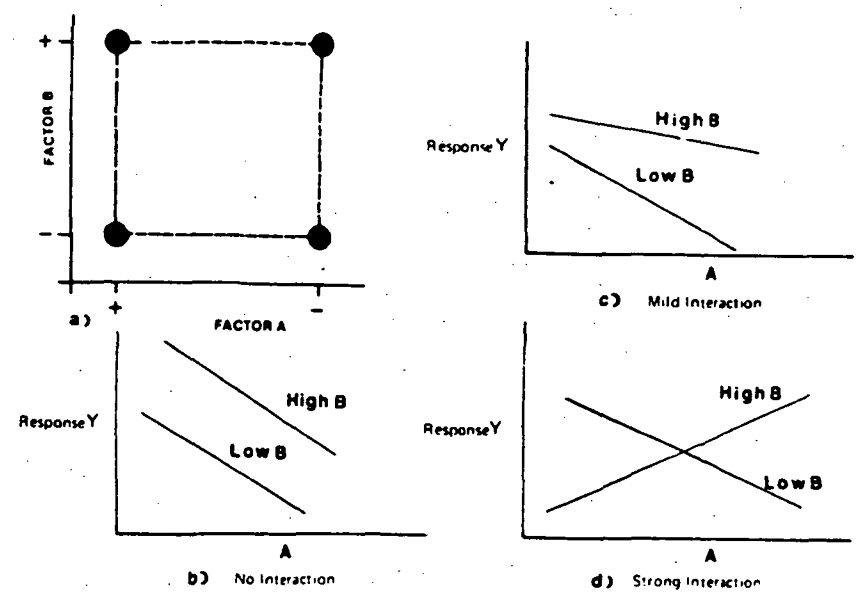


Fig. 1 (a) Experiment space for a two-factor experiment. (b - d) Interaction of A and B: (b) no interaction; (c) mild interaction; (d) strong interaction.

Computing Table for Analyzing Factorial Designs with 2 to 4 Factors

RUN	Mean	x_1	x_2	x_1x_2	x_3	x_1x_3	x_2x_3	$x_1x_2x_3$	x_4	x_1x_4	x_2x_4	$x_1x_2x_4$	x_3x_4	$x_1x_3x_4$	$x_2x_3x_4$	$x_1x_2x_3x_4$
1	+	-	-	+	-	+	+	-	-	+	+	-	+	-	-	+
2	+	+	-	-	-	-	+	+	-	+	-	+	+	-	+	-
3	+	-	+	-	-	+	-	+	-	+	-	+	+	-	+	-
4	+	+	+	+	-	-	-	-	-	-	-	-	+	+	+	+
5	+	-	-	+	+	-	-	+	-	+	+	-	-	+	+	+
6	+	+	-	-	+	+	-	-	-	-	+	+	-	-	+	+
7	+	-	+	-	+	-	+	-	-	+	-	+	-	-	+	+
8	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-
9	+	-	-	+	-	+	+	-	+	-	-	+	-	+	+	-
10	+	+	-	-	-	-	+	+	+	+	-	-	-	-	+	+
11	+	-	+	-	-	+	-	+	+	-	+	-	-	+	-	+
12	+	+	+	+	-	-	-	-	+	+	+	+	-	-	-	-
13	+	-	-	+	+	-	-	+	+	-	-	+	+	-	-	+
14	+	+	-	-	+	+	-	-	+	+	-	-	+	+	-	-
15	+	-	+	-	+	-	+	-	+	-	+	-	+	-	+	-
16	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

FILM DIAGNOSTICS

As mentioned before, various measurements are made.

1. Fourier Transform Infra-Red (FTIR) spectroscopy (transmittance spectroscopy) measurements are done with a Nicolet DX 10 model FTIR machine. The objective of this measurement is to determine both the hydrogen content and the silicon-hydrogen bond configurations. The dihydride (SiH_2) bonding has been known to cause poor film quality. So, by finding the ratio of the monohydride-to-dihydride, we can have a good indicator of the quality of the film; the ratio should be as high as possible. Two absorption peaks commonly used to determine the dihydride mode are 875 cm^{-1} (bending) and 2090 cm^{-1} (stretching). We used the peak at 2090 cm^{-1}. The monohydride (SiH) peak at 2000 cm^{-1} (stretching) is used.

At first we deposited the a-Si:H on an aluminum foil, hoping to separate the film from the foil by etching away the foil with HCL acid. If this is possible, for sure there will be no interference from the substrate during the FTIR measurements. This method was successfully applied on silicon nitride film. However, our attempt on a-Si:H failed, as we believe aluminum degrades the film. So, we resorted to using the crystalline silicon for substrate. Figure (2) and Figure (3) compare the spectrums of the absorption peaks. The Figure (2) indicates a poorer quality film (a-Si:H i-layer), and Figure (3) indicates a much improved quality material.

2. Visible spectrophotometry is done on a Cary 210 spectrophotometer. This measurement is used to determine the optical band gap (Tauc) of the films. Wavelengths from 400 nm to 750 nm are scanned. The spectrophotometer

FIGURE 2 : FTIR SPECTRUM SHOWING HIGHER SiH_2/SiH RATIO

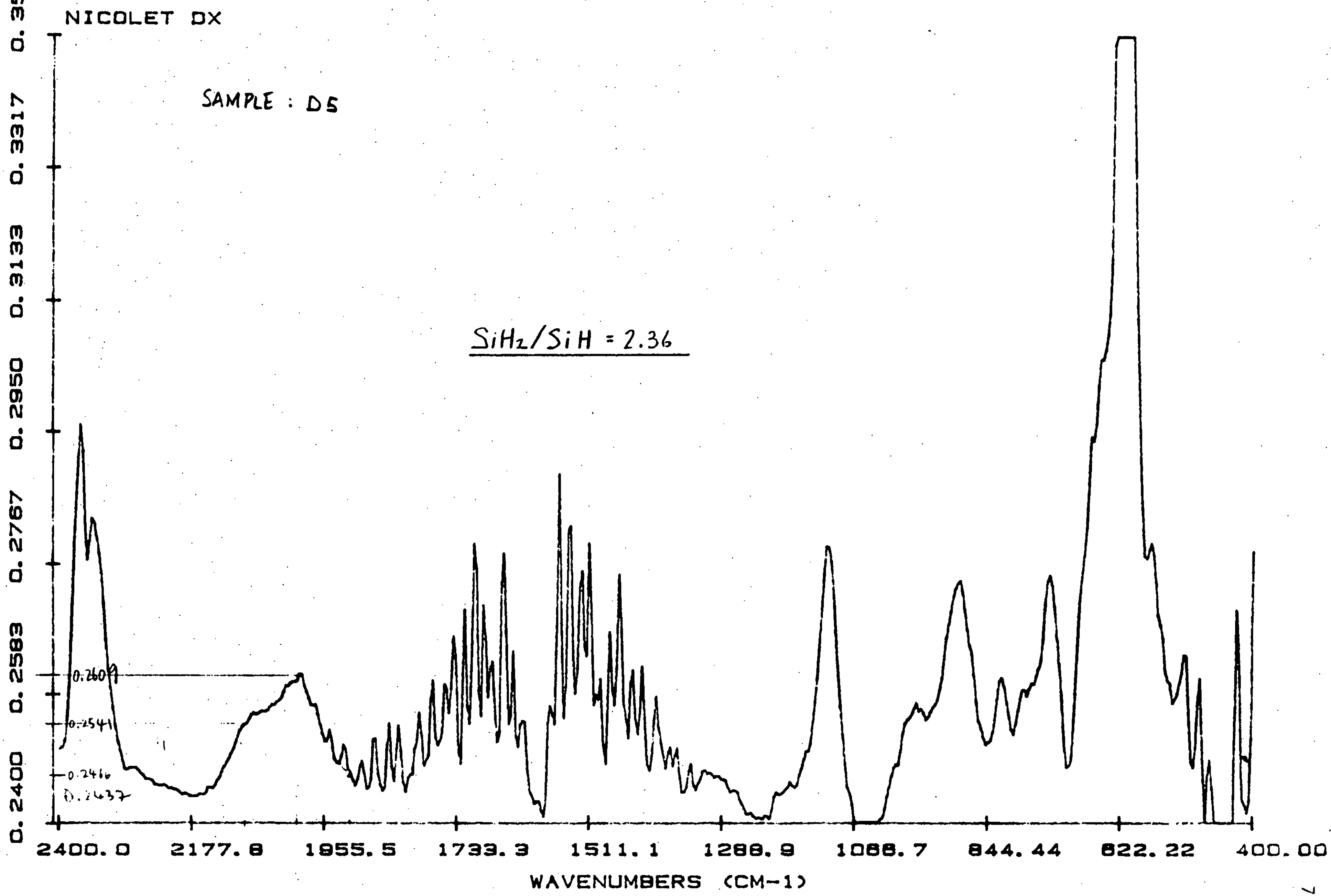
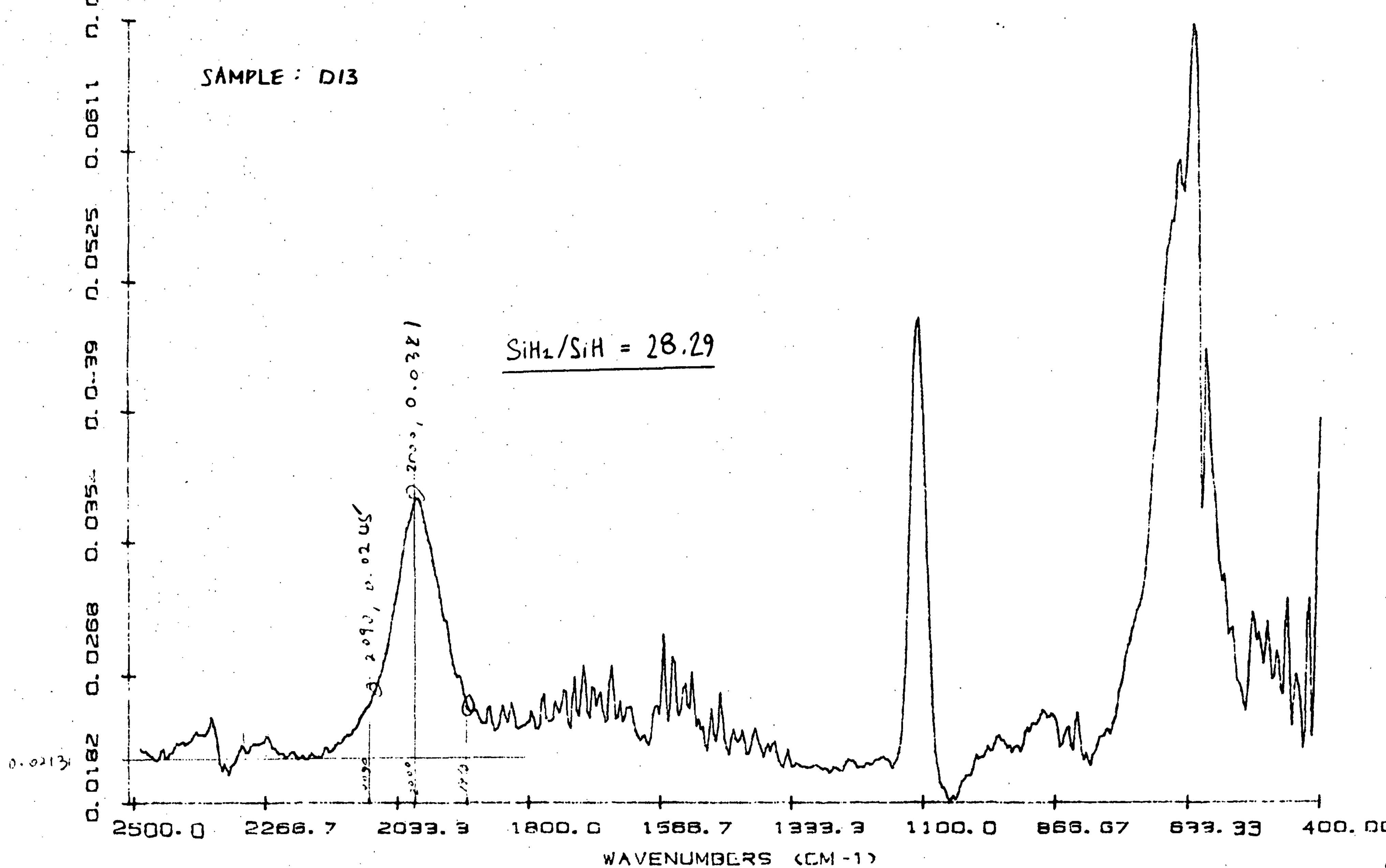


FIGURE 3. FTIR SPECTRUM SHOWING LOWER SiH_2/SiH RATIO



plots the absorbance against the wavelength. A typical plot is shown in Figure (4). The absorption coefficient α is chosen such that it is greater than 10^4 cm^{-1} so that the solar spectrum can be absorbed [3]. Figure (4) is interpolated, and the data is used to plot the square root of the product of the absorption coefficient and the photon energy [$\sqrt{(\alpha h\upsilon)}$] against the photon energy [$h\upsilon$]. The intersection of that function with the x-axis gives the optical band gap. Also, the slope of this function can be used to characterize disorder in amorphous silicon-based alloys. Figure (5) shows a regressed plot of sample I9 having a band gap, Eg=1.737, and Figure (6) shows a plot of sample D3 having a band gap, Eg=1.621.

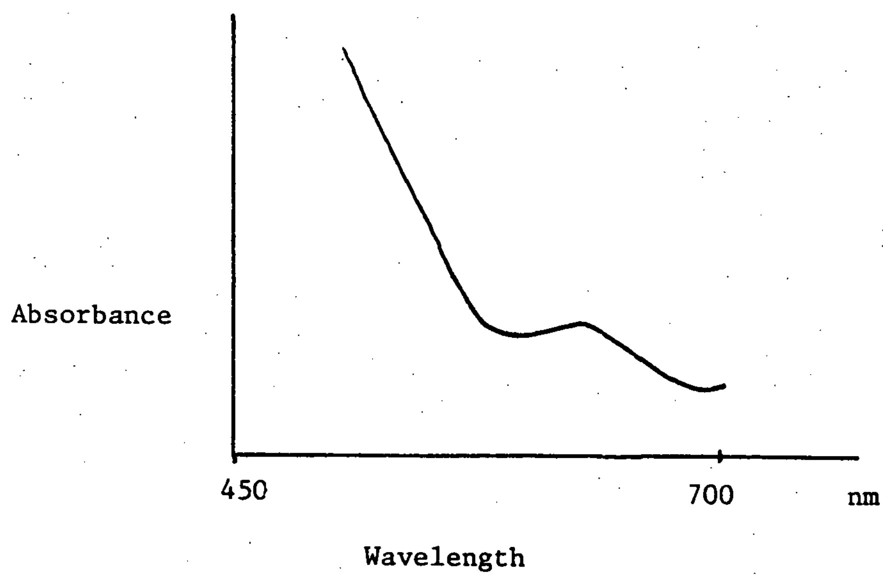
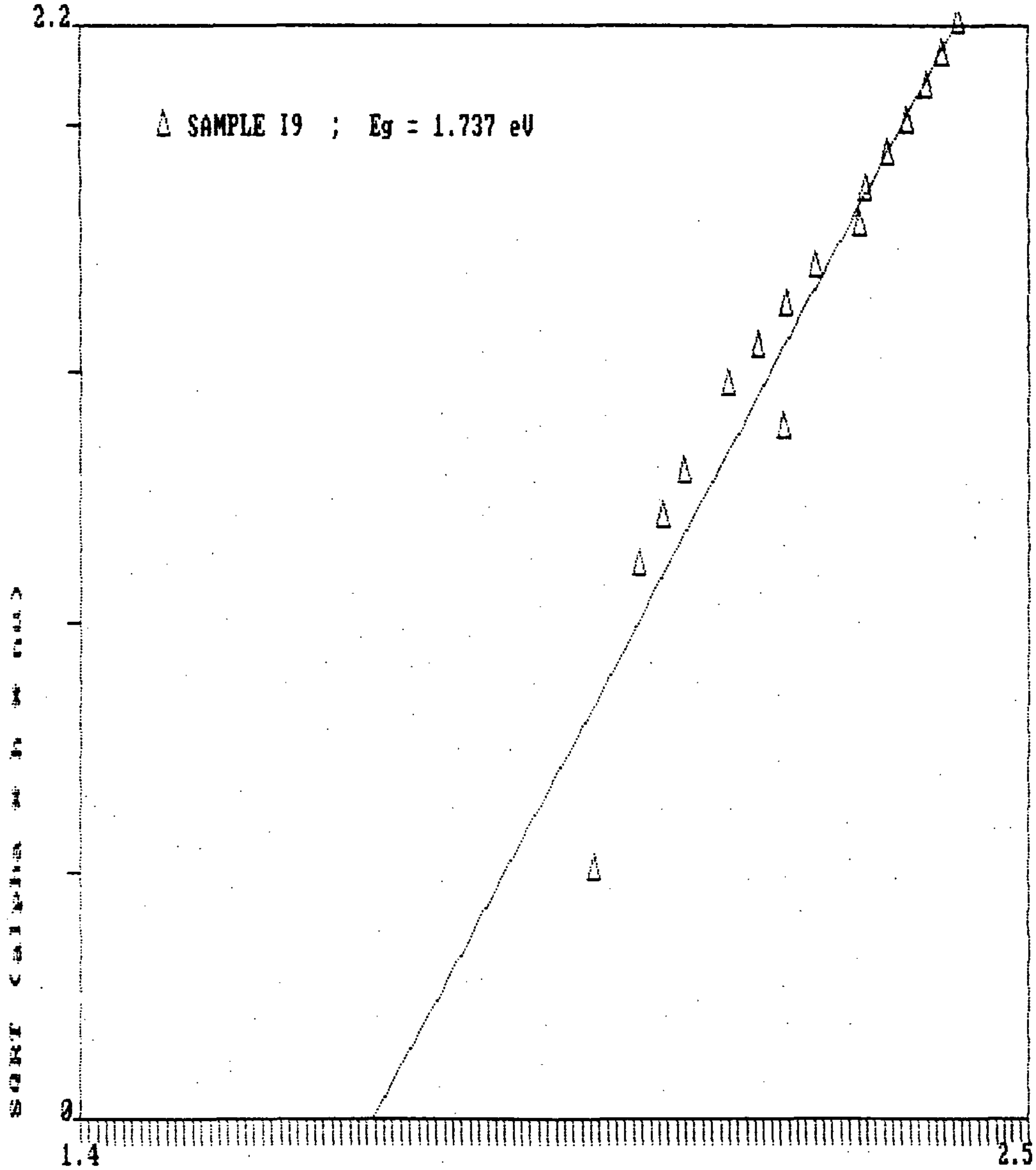


FIGURE 4

3. Both the photo- and dark conductivity measurements are done with the HP-4154A semiconductor parameter analyzer. Initially the vertical geometry is used, and the contacts are thermally evaporated aluminum and indium. We faced surface field effect and non-ohmic problems with both metals. Then the

FIGURE 5. TAUC OPTICAL BAND GAP



THE REGRESSION POLYNOMIAL OF LINE 1 -

(-5.660E+00) + (3.259E+00)*X
THE VARIANCE - 1.317E-02

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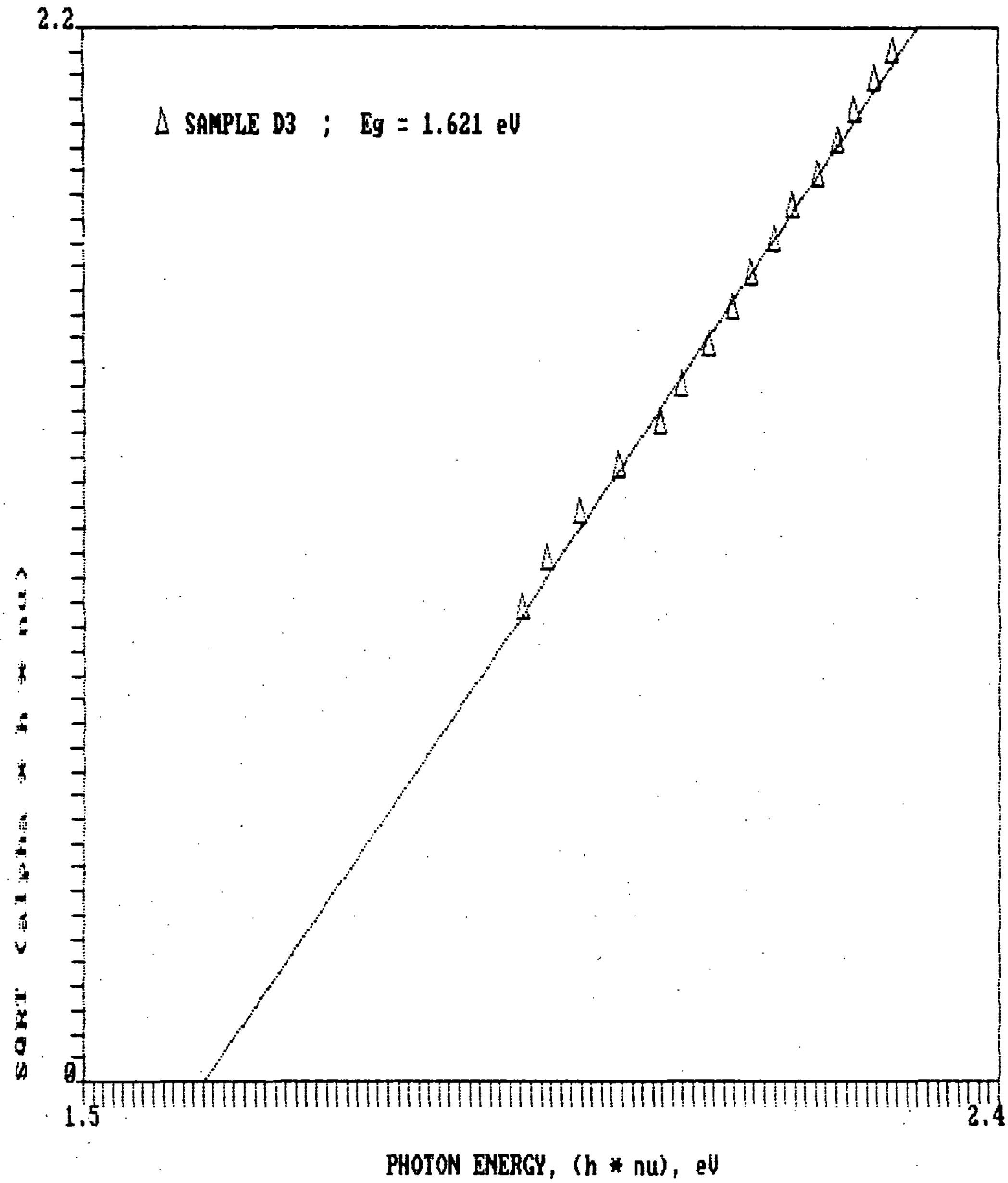
OF POOR QUALITY

D

FIGURE 6. TAUC OPTICAL BAND GAP



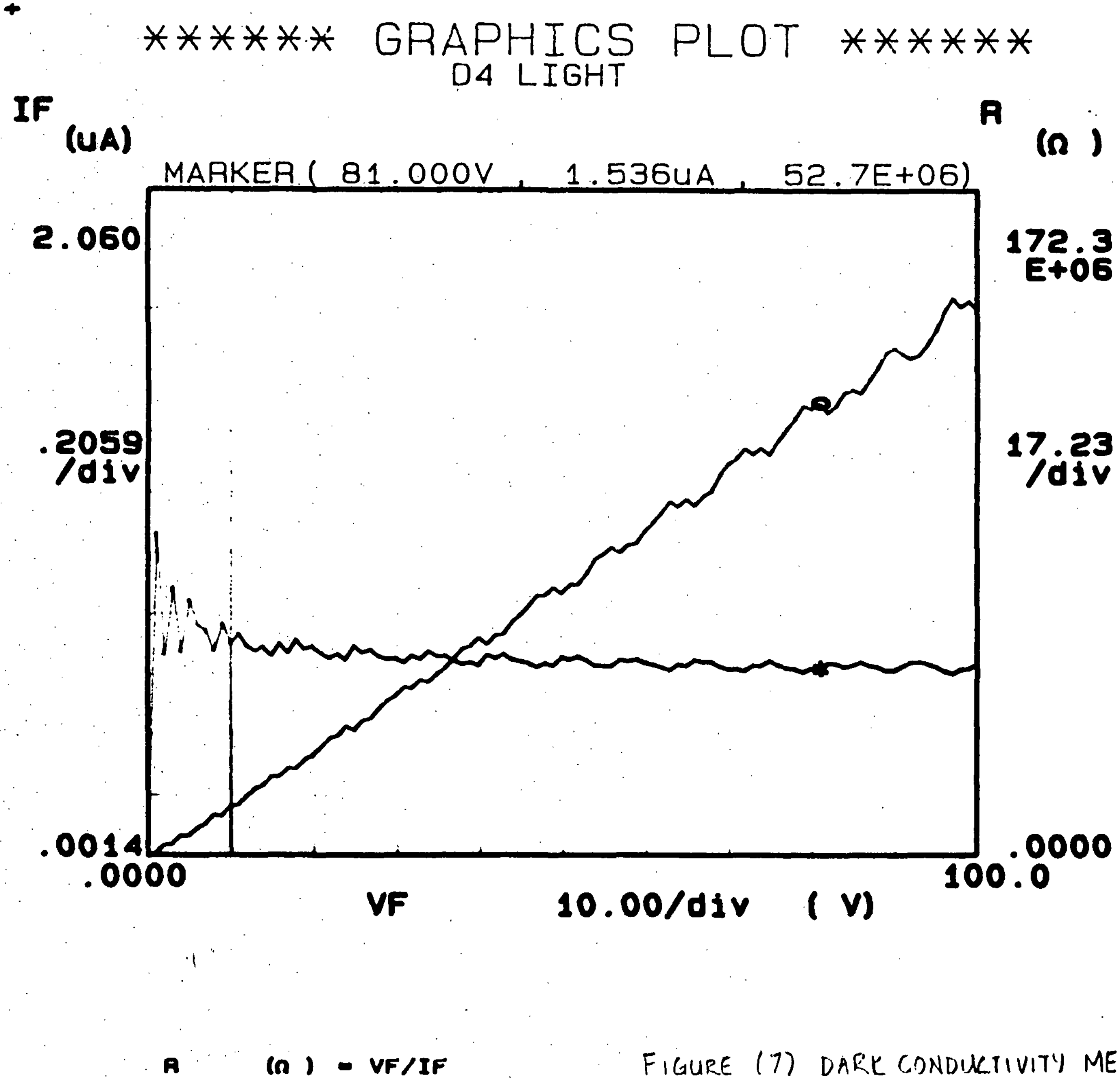
THE REGRESSION POLYNOMIAL OF LINE 1 -

(-5.090E+00) + (3.141E+00)*X
THE VARIANCE - 3.701E-04

planar geometry is used for the conductivity measurements [4]. Silver paint is used as contact. Two one-centimeter strips are painted one millimeter apart. Copper wires are applied on top of the silver paint [5]. A voltage of one hundred volts is swept through one of the terminals and current in the picoamps is obtained. For the photoconductivity measurement, AM1.5 of light is supplied by an ELH bulb. Figure (7) shows a dark measurement, and Figure (8) shows a light measurement. Also, the ratio of the photo- over the dark conductivity (photosensitivity) is calculated, which is a good indicator of the quality of the film.

4. Film thickness measurement is done using a monochrometer and an integrating sphere. Various wavelengths from 600 nm to 1100 nm is shone through the a-Si:H film; the power is then recorded. A plot of transmittance against the wavelength is drawn, as shown in figure (9). The distance between the two peaks is measured. Finally, the thickness is calculated using thickness, $d = m \times \lambda_1 \times \lambda_2 / 2 \times R.I. \times (\lambda_2 - \lambda_1)$ where, n=1 (next peak), λ_2 = peak on the right, λ_1 = peak on the left, and R.I.= refractive index.

5. Again with the monochrometer and the integrating sphere, the refractive index (R.I.) of the a-Si:H material is determined. The refractive index is 3.5.



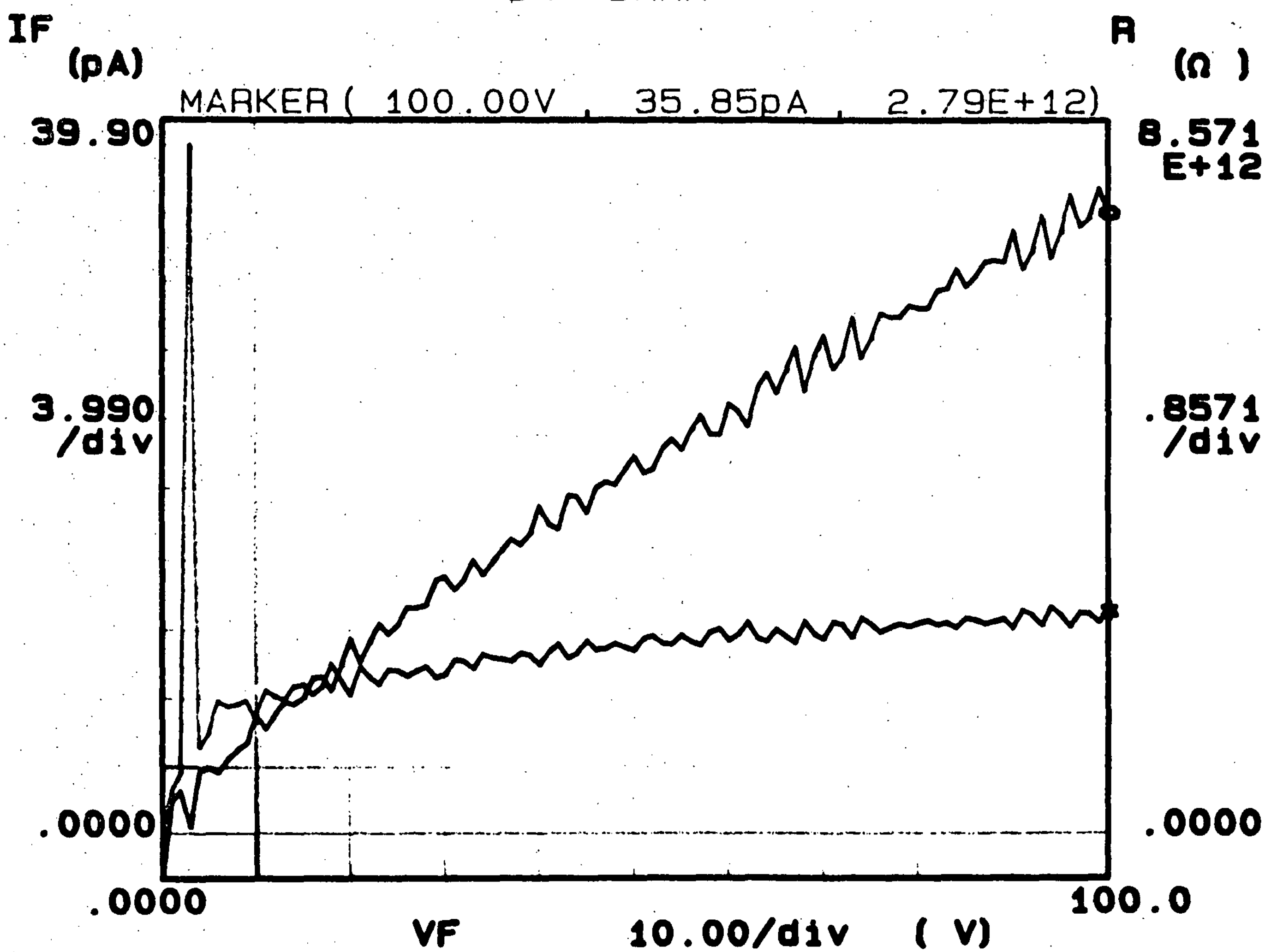
Variable1:
VF -Ch1
Linear sweep
Start .0000V
Stop 100.00V
Step 1.0000V

Constants:
V -Ch3 .0000V

FIGURE (7) DARK CONDUCTIVITY MEASUREMENT

****** GRAPHICS PLOT ******

D4 DARK



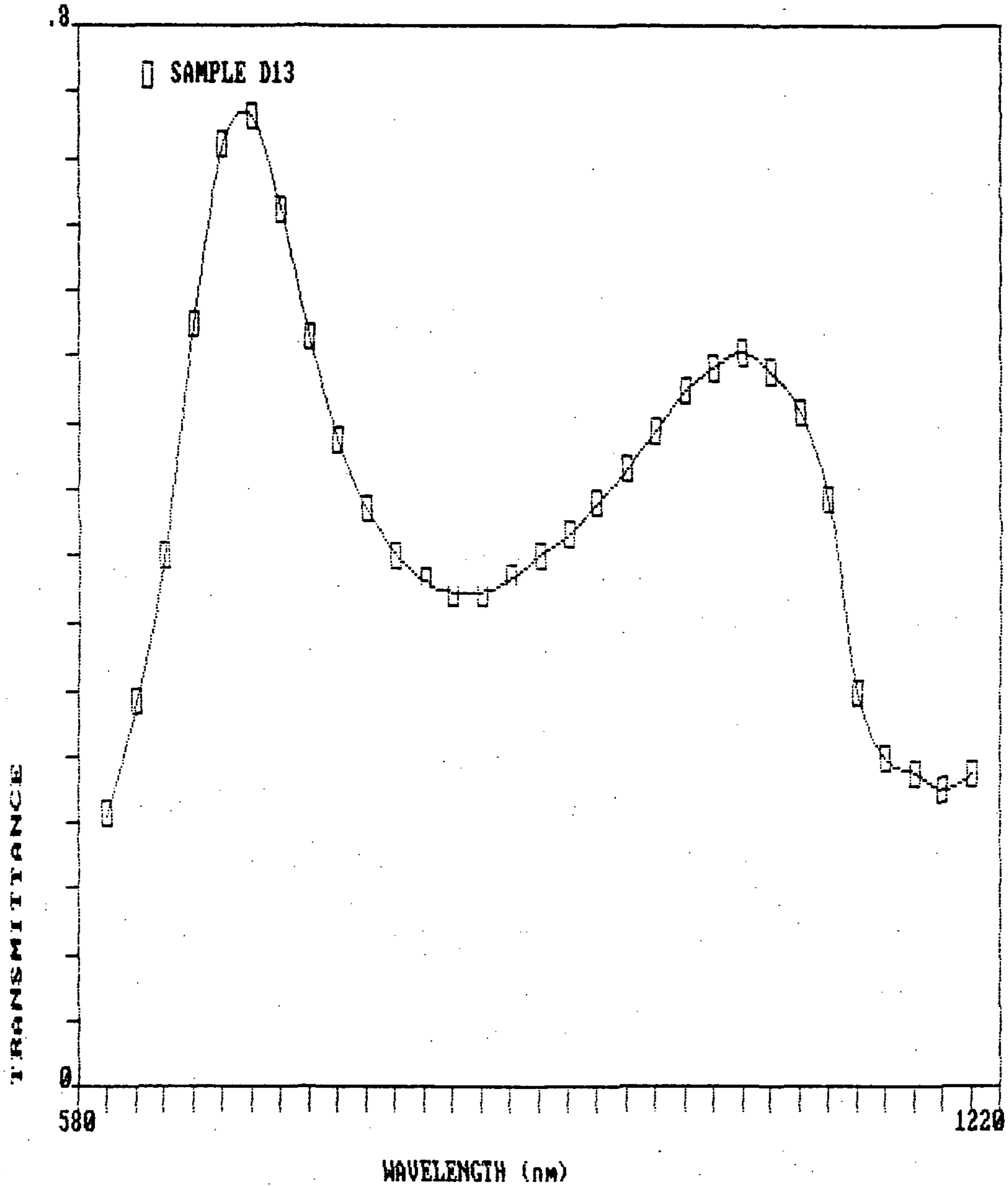
Variable1:
VF -Ch1
Linear sweep
Start .0000V
Stop 100.00V
Step 1.0000V

Constants:
V -Ch3 .0000V

R (Ω) = VF/IF

FIGURE (8) LIGHT CONDUCTIVITY MEASUREMENT

FIGURE 9. TRANSMITTANCE VS WAVELENGTH (FOR THICKNESS CAL.)



SUMMARY OF RESULTS FOR THE i-LAYER a-Si:H

Sam	Eg	SiH/SiH_2	Dk. COND	Lt. COND	Lt/Dk	D.R. (A/sec)	(T,Pr,F,Pwr)
D2	1.6357	33.900	5.36E-10	9.30E-5	1.74E+5	2.986	(- - + +)
D3	1.7057	4.046	1.14E-10	5.53E-5	4.83E+5	4.029	(- + + +)
D4	1.6464	2.019	6.02E-10	3.45E-5	5.73E+4	2.008	(+ + + -)
D5	1.7149	2.362	2.92E-10	1.39E-5	4.76E+4	3.171	(- + + -)
D6	1.7057	44.345	2.28E-09	2.11E-5	9.24E+3	2.051	(+ - + -)
D7	1.6214	12.268	1.45E-09	2.19E-5	1.51E+4	2.111	(- + - +)
D8	1.6255	10.685	1.79E-10	8.16E-6	4.57E+4	1.857	(- - - -)
D9	1.6642	13.616	3.15E-10	9.09E-5	3.14E+5	3.148	(+ - - +)
D10	1.6900	21.624	9.35E-10	1.87E-4	2.00E+5	2.252	(+ + + +)
D11	1.5248	4.535	3.16E-09	5.63E-6	1.78E+3	1.826	(+ + - -)
D12	1.6810	9.084	2.09E-09	3.45E-6	1.65E+3	1.484	(- - + -)
D13	1.6242	22.931	1.58E-09	5.00E-5	3.18E+4	1.699	(+ - - -)
D14	1.6709	35.600	9.76E-09	1.91E-4	1.95E+4	2.612	(+ - + +)
D15	1.6620	11.285	1.94E-09	8.30E-5	4.27E+4	2.986	(- - - +)
D16	1.6395	14.640	4.54E-09	1.47E-4	3.24E+4	2.111	(+ + - +)
D17	1.5565	7.450	1.08E-09	3.39E-6	3.15E+3	1.320	(- + - -)

For above: T = temperature in °C; Pr = pressure in milli-torr
F = flow rate in sccm; Pwr= Power in milli-watts/cm^2

	temp	press	flow	pwr
(+)	250	600	45	30.8
(-)	230	500	30	21.6

PIN Solar Cells

From the table above, taking the light/dark conductivity ratio as the significant indicator, we chose sample D9's parameter to fabricate some p-i-n solar cells. We manage to obtain a high Voc of 0.845 volts in one cell and a high Jsc of 9.05 mA/cm^2 in another. These cells have average areas of 0.01767 cm^2. The highest efficiency obtained so far is about three percent.

Presently, we are plagued with low fill factors and low current densities.

The boron concentration in the i-layer is found to be a very important factor. By varying the pumping down time (removal of the diborane), after the deposition of the p+ layer, we obtained drastic changes in the efficiencies of the cells. Furthermore, the thickness of the p+ layer is found to also have a great impact on the efficiency. Just a mere 30 Angstroms or less in the thickness of the P+ layer, can affect the result tremendously. Also pure silver was found to give better contacts.

PLAN OF WORK (JUNE 1,1988 - SEPTEMBER 30, 1988)

We believe that the i-layer is of good solar grade, by virtue of the good Voc obtained. It is a matter of time before we combine the pieces together to obtain the recipe of trivial fabrication of >7 percent efficient solar cells. Right now, we have drafted a systematic plan to approach our goal:

1. About 2000 A° thick layers of boron-doped a-Si:H films will be deposited using various ratios of diborane to silane flow rates (from 0.3 - 1.0 vol.%) until an optimum dark conductivity of 10^{-3} - 10^{-4} S cm^{-1} is achieved.
2. Similar experiments will be repeated for the n+ layer to obtain dark conductivity of about 10^{-2} S cm^{-1}.
3. The efficiency (and Voc) of the solar cells fabricated on SnO:F coated 7059 glass will be maximize by decreasing the thickness of the p+ layer from an initial value of 150 A°. The n+-layer thickness will be kept constant during these experiments. The chamber will be pumped down for a fixed amount of time after the p+ deposition before starting the i-layer

deposition.

4. The pump down time after the p+ layer deposition will be varied to maximized the efficiency.
5. The n+ layer thickness will then be optimized.
6. The i-layer thickness may be optimized.

For the phase three study of the degradation phenomena, the detail plan is listed in the new proposal for the next fiscal year. Briefly, in this phase, we will investigate whether this degradation is of extrinsic in nature (elemental). ZnO:F as a TCO has been shown to be more stable than ITO, in terms of being reduced to its elemental metallic nature, in the silane plasma. Trace amount of silver will be introduced into the ZnO:F layer and its effect studied. An economical spray pyrolysis deposition system for ZnO:F films will be set up. Other metals such as Au, Pt, and Cu may also be incorporated to further the study.

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